METHOD OF GROWING ORIENTED CALCIUM FLUORIDE SINGLE CRYSTALS

Cross-Reference to Related Applications

[0001]   This application claims priority from U.S. Provisional Application No 60/408,154, filed September 3, 2002, entitled "A Method to Grow [100] Oriented CaF_2 Single Crystals" and from U.S. Provisional Application No 60/408,116, filed September 3, 2002, entitled "A Method to Grow [110] Oriented CaF_2 Single Crystals."

Background of Invention

[0002]   Microlithography is used in semiconductor manufacturing to define patterns on integrated circuits. A microlithography system includes an illumination system and a projection system. The illumination system typically includes an excimer laser, which is used to irradiate a mask containing a circuit pattern. The projection system typically includes several projection lenses with highly complex objectives for imaging the circuit pattern onto a wafer. The smallest feature size, F, that can be imaged is determined by the following expression:

$$F = \frac{k_1 \lambda}{NA} \tag{1}$$

where k_1 is a process-dependent parameter, typically having a value of 0.5, λ is the illumination wavelength, and NA is the numerical aperture of the objective. From equation (1), the resolution of the microlithography system, i.e., the smallest feature size that can be imaged, can be increased by decreasing the illumination wavelength, λ, and/or increasing the numerical aperture, NA. However, because the depth of focus decreases as numerical aperture increases, it is usually easier to increase resolution by decreasing illumination wavelength.

[0003]   The industry presently uses 248-nm microlithography systems to image feature sizes larger than 0.25 μm and is preparing to transition to 193-nm microlithography systems that can image feature sizes 0.25 μm and smaller. The industry is also actively developing 157-nm

microlithography systems to image feature sizes as small as 100 nm. Successful transition to the 193-nm systems and development of the 157-nm systems depend on the availability of lens materials with high transparency at these wavelengths as well as low birefringence, low residual index inhomogeneity, low anisotropy, and ability to withstand prolonged irradiation without changes in optical properties. Unfortunately, there are not many lens materials that meet these requirements at wavelengths below 200 nm. Fused silica, which is used as lens material in the 248-nm microlithography system, can be used in 193-nm microlithography, although the safety margin for absorption at this wavelength is very small. Fused silica is not transparent enough to be used in 157-nm microlithography.

[0004]   Up to date, calcium fluoride (CaF_2) single crystal is the most viable lens material for 157-nm microlithography. CaF_2 has high transparency at this wavelength and the ability to withstand prolonged irradiation at this wavelength without its optical properties changing. As a cubic crystalline material, a CaF_2 single crystal is generally presumed to be isotropic and non-birefringent. However, recent findings indicate that a CaF_2 single crystal has anisotropic, birefringent behavior at short wavelengths because of symmetry-breaking. According to Burnett *et al.*, intrinsic birefringence in CaF_2 single crystal at 157 nm is 11.2 ± 0.4 nm/cm in the [110] direction, which is more than ten times the 1 nm/cm target birefringence for 157-nm microlithography. (Burnett, John. H., Levine, Zachary. H., & Shirley, Eric. L. "Intrinsic Birefringence in Crystalline Optical Materials: A New Concern for Lithography." Future FAB International 12 (2002): 150-154.) Fortunately, intrinsic birefringence has symmetry and specific orientations with respect to the crystallographic orientations, which can be exploited to achieve birefringence reduction. For example, intrinsic birefringence can be compensated for in lens design by combining and clocking [111]- and [100]-oriented CaF_2 single crystal lens elements. (Dana, Stephane. "Progress Report: 157-nm Lithography Prepares to Graduate." OE Magazine Feb. 2003: 12-14.) Intrinsic birefringence may also be compensated for in lens design by combining and clocking [100]- and [110]-oriented CaF_2 single crystal lens elements.

[0005]   From the foregoing, it is obvious that high-quality [111]-, [110]-, and [100]-oriented CaF_2 single crystals are needed to enable flexibility in microlithography lens design. [111]-oriented CaF_2 single crystals are readily available and are commonly grown using the Bridgman-Stockbarger process. The process involves a crucible containing CaF_2 feedstock in a

hot zone in a two-zone vertical furnace. A [111]-oriented seed crystal is mounted in a seed crystal holder at the bottom of the crucible with the upper portion of the seed crystal in contact with the feedstock. The crucible is heated to melt the feedstock. The crucible is then slowly lowered into a cold zone in the vertical furnace, the cold zone being at a lower temperature than the hot zone. As the crucible moves into the cold zone, the molten fluoride passes through a temperature gradient zone. A crystal front conforming to the crystallographic orientation of the seed crystal is created as the temperature of the molten fluoride drops below the melting point. The crystal propagates inside the crucible, within the molten fluoride, as long as the crucible continues to move downwardly into the cold zone. The crystal is usually annealed once the crucible is fully in the cold zone and/or post-annealed in a separate furnace to reduce stress-induced birefringence to an acceptable level.

[0006] Due to difficulty and low yield of [110]- and [100]-oriented CaF_2 single crystal growth, [110]- and [100]-oriented CaF_2 single crystals are usually made by cutting them out of [111]-oriented CaF_2 single crystals. This method of making [110]- and [100]-oriented CaF_2 single crystals is not only inefficient but also greatly limits the size of the [110]- and [100]-oriented lens elements that can be obtained and increases the cost of production. Another challenge for the [110]- and [100]-oriented CaF_2 single crystal growth is high stress-induced birefringence. Due to a higher stress optical coefficient in the [110] and [100] directions, [110]- and [100]-oriented CaF_2 single crystals are expected to yield a higher stress-induced birefringence. (Burnett, J. H., Levine, Z. H., & Shirley, E. L. Intrinsic Birefringence in Calcium Fluoride and Barium Fluoride. Physical Review B 64, 241102 (2001).) It would be beneficial to have the average stress-induced birefringence of [110]- and [100]-oriented CaF_2 single crystals be as low as that of the [111]-oriented CaF_2 single crystals. [111]-oriented CaF_2 single crystals with average stress-induced birefringence better than 1 nm/cm are now available.

[0007] From the foregoing, there is desired a method of economically growing CaF_2 single crystals along the [110] and [100] directions, respectively, the grown crystals preferably having stress-induced birefringence sufficiently low to allow their usage in making optical elements for 157-nm microlithography process.

Brief Summary of Invention

[0008]   In one aspect, the invention relates to a method of making oriented calcium fluoride single crystal which comprises loading calcium fluoride feedstock on top of a seed crystal having a specific crystallographic orientation, heating the calcium fluoride feedstock to a temperature sufficient to form a melt, and growing a calcium fluoride crystal on the seed crystal by progressively moving the melt and the seed crystal through a temperature gradient zone having an axial temperature gradient in a range from approximately 2°C/cm to approximately 8°C/cm, wherein a growth direction of the calcium fluoride crystal substantially conforms to the crystallographic orientation of the seed crystal.

[0009]   In another aspect, the invention relates to a calcium fluoride crystal for making optical elements for transmitting below 200-nm ultraviolet light having a [100] crystallographic orientation and a diameter greater than or equal to approximately 250 mm and exhibiting a mean birefringence no greater than approximately 1.2 nm/cm and inhomogeneity no greater than approximately 1.1 ppm.

[0010]   Other features and advantages of the invention will be apparent from the following description and the appended claims.

Brief Description of Drawings

[0011]   Figure 1A-1D illustrate a method of making [110]- and [100]-oriented calcium fluoride crystals according to an embodiment of the invention.

[0012]   Figure 2 is a graph showing centerline temperature and temperature gradient versus axial direction as crystal is formed.

[0013]   Figure 3 is a graph of an annealing and cooling profile for a calcium fluoride crystal according to an embodiment of the invention.

Detailed Description

[0014]   The invention will now be described in detail with reference to a few preferred embodiments, as illustrated in the accompanying drawings.   In the following description, numerous specific details are set forth in order to provide a thorough understanding of the invention.   It will be apparent, however, to one skilled in the art that the invention may be practiced without some or all of these specific details.   In other instances, well-known features and/or process steps have not been described in detail in order to not unnecessarily obscure the invention. The features and advantages of the invention may be better understood with reference to the drawings and discussions that follow.

[0015]   In the background discussion, the inventors mentioned that [110]- and [100]-oriented CaF_2 single crystals are usually cut out of [111]-oriented CaF_2 single crystals.   One would expect that like [111]-oriented CaF_2 single crystals, which are grown directionally using [111]-oriented seed crystals, it should be fairly straightforward to grow [110]- and [100]-oriented CaF_2 single crystals directionally using [110]- and [100]-oriented seed crystals, respectively. However, while not wishing to be bound by theory, the inventors argue herein that CaF_2 single crystals likely exhibit preferential growth in the [111] direction.   According to the general solidification theory, once a nucleus is formed, crystal growth is limited by (a) the kinetics of atom attachment to the solid-liquid interface, (b) capillarity, and (c) diffusion of heat and mass. (Kurz, W. & Fisher, D. J. Fundamentals of Solidification. Aedermannsdorf-Suitzerland: Trans Tech Publications, 1986.)   The relative importance of each of these factors depends on the substance in question and upon the growth conditions. For CaF_2 single crystals, growth in the [111] direction appears to be favored when the dominant control factor is kinetics of atom attachment to the liquid-solid interface or diffusion of heat and mass.

[0016] CaF_2 single crystal very likely grows with a microscopically faceted interface, which actually consists of many atomically-flat facets, due to its high (higher than metals) entropy of fusion. These atomically-flat facets generally choose a low-index plane with the lowest interface energy. As a result, the faceted growth mode tends to give different atomic attachment kinetics in different interface planes, and therefore might show an anisotropy in growth velocity for different orientations. Since CaF_2 crystals exhibit (111)-faceted surfaces it is

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reasonable to assume that the interface energy and attachment rate of CaF_2 are lowest in the (111) planes. From the standpoint of atomic attachment kinetics, it means that CaF_2 has very slow (axial) growth rate in [111] direction and very quick spreading (radial) speed in (111) plane. The growth in the [111] direction looks like layer-by-layer spreading in (111) plane. This growth mode makes it easier to maintain [111] orientation because any nucleation and growth in other directions will be suppressed by the rapid spreading (radial growth) in (111) plane.

[0017]   However, growth in the [110] or [100] direction shows a different behavior from the one described above for the [111] direction in that the axial growth rate along the [110] or [100] direction could be higher than the radial growth rate along the solid-liquid interface. The slower radial growth will make the nucleation in other directions easier to propagate into the [110] or [100] direction and result in loss of singularity. It should be pointed out that this mechanism is applicable only for those growth processes where kinetics of atom attachment to the liquid-solid interface is the dominant control factor. From the point of view of diffusion of heat and mass, growing CaF_2 crystals along the [111] direction should also be easier than growing along the [110] or [100] direction. According to McCurdy, the thermal conductivity of CaF_2 is highest along the [111] direction and lowest along the [100] direction, with the difference being as much as 40% (McCurdy, A. K. "Phonon Conduction in Elastically Anisotropic Cubic Crystals." Physical Review B 26 (1982): 6971.) This suggests that [111] might be the preferential direction for growing CaF_2 crystals.

[0018]   Embodiments of the invention provide a method of encouraging CaF_2 single crystal growth in or "near" the [110] or [100] direction. "Near" could be 3 to 5 degrees from the [110] or [100] direction but is preferably less than 1 degree from the [110] or [100] direction. The CaF_2 single crystals grown by the method of the invention have low stress-induced birefringence and low residual index inhomogeneity and can be used for making optical elements for 157-nm microlithography process and below 200-nm microlithography processes in general. Referring to Figure 1A, the crystal growth process starts with a seed crystal **100** having [110] or [100] crystallographic orientation. A [110]-oriented seed crystal is used to grow [110] crystals, and a [100]-oriented seed crystal is used to grow [100]-oriented crystals. Typically, the seed crystal **100** is CaF_2 crystal. However, it may also be possible to use SrF_2 crystal or other materials having a similar phase and melting point to CaF_2. The seed crystal **100** is placed in a

seed crystal holder **102** at the base of a crucible **104**. In the illustrated embodiment, the crucible **104** has multiple crystal growth chambers **106**. The crucible **104** may have any number of crystal growth chambers, typically in a range from 1 to 20. The crystal growth chambers **106** are in communication through holes **108** in the crystal growth chambers **106**.

[0019] Each crystal growth chamber **106** contains CaF_2 feedstock **110**. Preferably, the feedstock **110** is pretreated to remove impurities such as oxides that can have a detrimental effect on the optical performance of the grown crystal. An oxide scavenger may also be mixed with the feedstock **110**. The crucible **104** with the feedstock **110** is supported in a vertical furnace **112**. The vertical furnace **112** has a melting chamber **114** and an annealing chamber **116**. Heaters **118, 120** are disposed in the melting and annealing chambers **114, 116**, respectively, to maintain a prescribed temperature profile inside the melting and annealing chambers **114, 116**. Insulation **122** may be provided around the heaters **118, 120** to assist in controlling the temperature in the melting and annealing chambers **114, 116**. An annular diaphragm **124**, made of insulating material, partially isolates the melting chamber **114** from the annealing chamber **116**, creating a temperature gradient zone **125** between the melting chamber **114** and the annealing chamber **116**. A lift mechanism **126** is coupled to the crucible **104**. As an example, the lift mechanism **126** could be a fluid-powered actuator, such as a hydraulic or pneumatic actuator, or a mechanical actuator. The lift mechanism **126** can be operated to move the crucible **104** along the axial length of the furnace **112**.

[0020] In one embodiment, temperature probes **128, 130** are provided inside the melting chamber **114** and annealing chamber **116**, respectively. In operation, the output of the temperature probes **128, 130** may be supplied to a control system (not shown) that will automatically adjust the input to the heating elements **118, 120** such that a desired temperature profile is maintained in the melting and annealing chambers **114, 116**. Preferably, the heaters **118, 120** can be controlled independently to achieve the desired temperature profiles inside the melting and annealing chambers **114, 116**, respectively. The heaters **118, 120** may be made of a single heating element or multiple heating elements. Various alternate heater configurations are possible. See, for example, U.S. Patent No. 6,562,126 (issued to Price) for possible alternate configurations.

[0021] In operation, the furnace 112 is hermetically sealed with vacuum, inert, fluorinating or other atmosphere suitable for crystal growth. The melting chamber 114 is then heated to a temperature sufficient to melt the feedstock 110 in the crucible 104, as shown in Figure 1B. For example, for CaF_2, the temperature is typically set at about 1500°C. The crucible 104 with the molten feedstock 110 is slowly translated from the melting chamber 114, through the diaphragm 124, into the annealing chamber 116. The annealing chamber 116 is maintained at a temperature lower than the temperature of the melting chamber 114 so that there is a temperature gradient across the diaphragm 124. As shown in Figure 1C, as the crucible 104 passes through the diaphragm 124, the molten feedstock 110 goes through the temperature gradient zone 125. As the crucible 104 passes through the temperature gradient zone 125, the temperature transition inside the molten feedstock 110 creates a solid-liquid growth front 134. The solid-liquid growth front 134 propagates inside the crucible 104, within the molten material 110, as long as the crucible 104 continues to move downwardly into the annealing chamber 116 to form crystal 132, which conforms to the crystallographic orientation of the seed crystal 100. In order to secure crystal growth in the orientation of the seed crystal 100, an initial position of the crucible 104 should be established so that the seed crystal 100 is partially, preferably half, melted prior to growing the crystal on the seed crystal.

[0022] The method of the invention is based in part on a contradictory fact about temperature gradient in crystal growth: high axial temperature gradient is good for growing crystals and bad for reducing stress-induced birefringence. This issue is particularly delicate for [110]- and [100]-oriented CaF_2 crystal growth because while the growth in these directions seems more difficult and therefore needs higher axial temperature gradient to ensure the singularity, the higher stress optical coefficient in these directions requires lower temperature gradient to produce a low stress-induced birefringence. It has been demonstrated that growing [110]- and [100]-oriented crystals under an axial temperature gradient above 1°C/cm, especially above 4°C/cm, is particularly preferred. It has also been demonstrated that the upper limit for growing [110]- and [100]-oriented single crystals with reduced stress-induced birefringence is 8°C/cm, preferably 6°C/cm. Combining these two opposite effects of axial temperature gradient on the singularity and stress-induced birefringence, a desired temperature gradient for growing

[110]- and [100]-oriented crystals with a low stress birefringence is 2°C/cm to 8°C/cm, preferably 2°C/cm to 6°C/cm, more preferably 3°C/cm to 5°C/cm.

[0023]   Figure 2 is an example of a graph showing centerline temperature and temperature gradient as a function of axial direction as the crystal is grown. The zero position on the axial direction axis corresponds to the solid-liquid interface (134 in Figure 1C). Returning to Figure 1C, the probability of obtaining [110] or [100] crystals is enhanced when the solid-liquid interface is within, preferably in the middle of, the insulation (diaphragm 124) zone. By doing this, the stress-induced birefringence and small-angle grain boundaries can be reduced. The solid-liquid interface can be constrained within the insulation zone by appropriately choosing the temperature set-points of the melting chamber 114 and the annealing chamber 116. The axial temperature gradient is largely controlled by the temperatures of the melting chamber 114 and the annealing chamber 116 as well as the configuration of the furnace 112, the length of the insulation (diaphragm 124) zone, and the material and size of the crucible 104. For the temperature gradient at the solid-liquid interface 134, the growth velocity also has an effect. The temperature gradient in the crystal tends to increase with the growth velocity due to the latent heat released during solidification. However, this effect could be negligible if the translation speed of the crucible 104 during crystal growth is below 3 mm/hr. Preferably, the translation speed of the crucible 104 is in a range from 0.5 mm/hr to less than 3 mm/hr. Preferably, the translation speed does not vary by more than 0.1 mm/hr.

[0024]   For illustration purposes, 300-mm diameter [110]- and [100]-oriented CaF$_2$ crystal growth experiments were carried out separately in a vertical Bridgman furnace. The feedstock was first mixed with scavengers and then put in a graphite crucible with a [110]-oriented CaF$_2$ seed crystal for [110] crystals and a [100]-oriented CaF$_2$ seed crystal for [100] crystals. The axial temperature gradient and the growth rate were set at around 6°C/cm and less than 3 mm/hr, respectively. Under these growth conditions, [110]- and [100]-oriented single crystals were successfully obtained. The crystals were cooled down using a conventional annealing process, typically including a rapid cooling rate of 6°C/hr from about 1500°C down to about 1100°C, a slow cooling rate of about 1.5°C/hr from about 1100°C down to about 750°C, an increased cooling rate of about 5°C/hr from about 750°C to about 450°C, and an even faster

cooling rate of 10°C/hr from about 450°C to about 20°C. Table 1 below shows the inhomogeneity and birefringence measurements for the crystals.

Table 1

Crystal Orientation	Birefringence (nm/cm)		Inhomogeneity (ppm)	
	Mean	RMS	with Power	without Power
[110]	5.8	6.6	3.2	1.4
[100]	8.2	12.5	3.7	3.5

[0025]   The stress-induced birefringence shown in Table 1 for [110]- and [100]-oriented CaF_2 single crystals is relatively high in comparison to that of [111]-oriented CaF_2 single crystals. The stress-induced birefringence of the [110]- and [100]-oriented CaF_2 single crystals could be reduced by growing the crystals at a lower axial temperature gradient and/or using an improved annealing process. A separate annealing process can also be used to reduce the birefringence in the crystals.

[0026]   In one embodiment, an in-situ annealing method is used to cool the crystals once the crucible 104 is fully inside the annealing chamber 116, as shown in Figure 1D. The in-situ annealing method uses two temperature regimes to cool down the crystal. The first temperature regime is between the melting temperature (approximately 1420°C) and approximately 1200°C. In this temperature regime, a decreasingly fast cooling profile and an increasingly slow cooling profile are applied to the melting chamber 114 and the annealing chamber 116, respectively, to reduce or diminish the temperature difference between the melting chamber 114 and the annealing chamber 116 which is required for crystallization. This temperature difference is preferably less than 50°C, more preferably less than 30°C, at the first temperature regime. This step is designed to minimize the temperature gradient in the annealing chamber 116 as early as possible. After the primary cooling stage, a substantially constant cooling rate is applied to both zones from the first temperature (in a range from about 1300°C to 1100°C, preferably in a range from about 1250°C to 1150°C) to a final temperature in a range from about 300°C to about 20°C, more preferably to room temperature. As shown in Figure 3, both cooling curves should be as smooth as possible to avoid any undesirable thermal disturbance. For crystals with a diameter greater than 250 mm, it has been demonstrated that desirable inhomogeneity and birefringence

can be achieved using a cooling rate of less than 3°C/hr, preferably 2°C/hr or less in the linear portion of the annealing.

[0027]   For illustration purposes, 300-mm diameter [100]-oriented CaF_2 crystal growth experiments were carried out in a vertical furnace. The feedstock was first mixed with scavengers and then put in a graphite crucible with a [100]-oriented CaF_2 seed crystal. The axial temperature gradient and the growth rate were set at around 6°C/cm and less than 3 mm/hr, respectively. Under these growth conditions, [100]-oriented single crystals were successfully obtained. The crystals were annealed in-situ using the linear annealing method described above. For the linear annealing method, the cooling rate after the initial cooling down of the melting and annealing chambers was approximately 2°C/hr. Table 2 below shows the inhomogeneity and birefringence measurements for the [100]-oriented single crystals.

Table 2

Annealing Method	Birefringence (nm/cm)		Inhomogeneity (ppm)	
	Mean	RMS	with Power	without Power
Linear	1.2	1.8	1.1	1.1
Conventional	8.2	12.5	3.7	3.5

[0028]   The invention provides one or more advantages. First, [110]- and [100]-oriented CaF_2 single crystals can be grown economically. Secondly, combining an appropriate annealing method with the crystal growth method of the invention allows [110]- and [100]-oriented CaF_2 single crystals having low birefringence and low inhomogeneity to be manufactured. With the in-situ annealing method described above, [110]- and [100]-oriented CaF_2 single crystals having low birefringence and low inhomogeneity can be grown in a single furnace run. The results above show that birefringence as low as 1.2 nm/cm has been achieved for [100]-oriented CaF_2 single crystals. Birefringence may be further reduced by choosing a lower temperature gradient and cooling rate for the crystal growth and annealing, respectively. Multiple crystals can be grown in a single furnace run using a multi-chamber crucible (or a stack of single-chamber crucibles) to increase the yield of the crystal growth process. The grown [110]- or [100]-oriented CaF_2 single crystals can be used to design lens systems for below 200 nm microlithography.

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[0029]   While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.